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THE CLEAVAGE OF CARBON—SULFUR AND CARBON—NITROGEN BONDS LEADING TO RHODIUM—THIOCARBOXAMIDO COMPLEXES

A.W. GAL*, A.F.J.M. VAN DER PLOEG, F.A. VOLLENBROEK and W. BOSMAN

Department of Inorganic Chemistry, Catholic University of Nijmegen, Toernooiveld, Nijmegen (The Netherlands)

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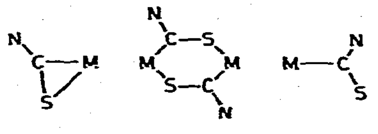
Summary

The cleavage of a C—S bond in methyl (*N,N*-dimethyl)dithiocarbamate, $MeSC(S)NMe_2$, by $RhCl(PPh_3)_3$ results in the formation of the methylsulfido-thiocarboxamido complex $RhCl(SMe)(SCNMe_2)(PPh_3)_2 \cdot C_6H_6$. The MeS group in this complex reacts with CS_2 to form the trithiocarbonato-thiocarboxamido complex $RhCl(S_2CSMe)(SCNMe_2)PPh_3$. Cleavage of the C—S bond in tetramethylthiurammonosulfide $Me_2NC(S)SC(S)NMe_2$ yields the dithiocarbamato-thiocarboxamido complex $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$. The analogous C—N bond breaking in 1,1,5,5-tetramethyl-3-phenyl-dithiobiuret, $Me_2NC(S)N(Ph)C(S)NMe_2$, results in the formation of $RhCl[N(Ph)C(S)NMe_2](SCNMe_2)PPh_3$. The crystal structure determination of chloro(*N,N*-dimethyldithiocarbamato)(*N,N*dimethylthiocarboxamido)triphenylphosphinerhodium(III) · chloroform reveals that the thiocarboxamido group is coordinated to Rh via a very short Rh—C bond (1.895 Å) and a much weaker Rh—S (2.432 Å) interaction.

Introduction

Thiocarboxamido complexes have recently been made via different preparative routes. Thus, addition of $MeNH_2$ to the thiocarbonyl group in $[(C_5H_5)Fe(CO)_2CS]^+$ leads to the formation of $(C_5H_5)Fe(CO)_2(SCNHMe)$ [1] and addition of HS^- to $[Pt(CNMe)_2(PPh_3)_2]^{2+}$ gives $[Pt(SCNHMe)(CNMe)(PPh_3)_2]^+$ [2].

The other reported thiocarboxamido complexes have been synthesized by oxidative addition of $Me_2NC(S)Cl$ to Rh^I, Ni^0 [3] and Pt^0, Pd^0 [4] phosphine complexes and to some manganese and molybdenum carbonyls [5]. Three types of coordination were shown to be possible: a side-on coordination via carbon and sulfur (I), coordination via carbon and sulfur as a bridge (II) and coordination via carbon (III) (Fig. 1).



(I) (II) (III)

Fig. 1. Types of coordination for the thiocarboxamido group.

Crystallographic evidence showed that $[(MeO)_3P]_2Pd_2Cl_2[SCNMe_2]_2$ (II) is dimeric via two C—S bridges [6]. Crystallographic evidence for a side-on thiocarboxamido group was found in the case of $[Mo(SCNPr_2)(S_2CNPr_2)S]_2$ [7]. This compound results from reaction of the *N,N*-dipropyldithiocarbamate ion with molybdenum(II) acetate, in which a formal oxidative addition of a C—S bond to the dithiocarbamate ion is involved.

We have investigated the possibility of using oxidative addition of the C—X bond in different organic molecules containing the *N,N*-dimethylthiocarboxamido group, $Me_2NC(S)X$ (in which X = SMe, $SC(S)NMe_2$ and $N(Ph)(C(S)NMe_2)$ to synthesize some new organometal complexes containing a thiocarboxamido group together with N- or S-coordinating ligands.

Experimental

Chloromethylsulfido (N,N-dimethylthiocarboxamido)-bis(triphenylphosphine)-rhodium(III) (complex I)

The complex $RhCl(PPh_3)_3$ reacts at room temperature in benzene under nitrogen with a stoichiometric amount of methyl (*N,N*-dimethyl)dithiocarbamate. After half an hour the beige air-stable complex $RhCl(SMe)(SCNMe_2)(PPh_3)_2 \cdot C_6H_6$ precipitates. This is washed with n-hexane and dried under vacuum. (Anal.: found: C, 63.0; H, 5.3; N, 1.5. $C_{46}H_{45}ClNP_2RhS_2$ calcd.: C, 63.0; H, 5.2; N, 1.6%.)

Chloro(N,N-dimethyldithiocarbamato)(N,N-dimethylthiocarboxamido)triphenylphosphinerhodium(III) (complex II)

The same procedure with $RhCl(PPh_3)_3$ and tetramethylthiurammonosulfide, involving stirring for one night, precipitation with n-hexane and drying under vacuum, gives the orange air-stable complex $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$. (Anal.: found: C, 49.3; H, 4.7; N, 4.5. $C_{24}H_{27}ClN_2PRhS_3$ calcd.: C, 47.3; H, 4.5; N, 4.6%. Mol. wt. osmometrically in $CHCl_3$, found: 586, calcd.: 609.)

Recrystallization from $CHCl_3$ or $CHCl_2$ solutions with n-hexane gives orange-red crystals of the solvent adduct, e.g. $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3 \cdot CH_2Cl_2$. (Anal.: found: C, 43.5; H, 4.2; N, 4.1. $C_{25}H_{29}Cl_3N_2PRhS_3$ calcd.: C, 43.3; H, 4.2; N, 4.0%.)

Chloro(N,N-dimethyl-N′-phenyl-thioureido)(N,N-dimethylthiocarboxamido)triphenylphosphinerhodium(III) (complex III)

The same procedure but using 1,1,5,5-tetramethyl-3-phenyl-dithiobiuret results in the orange air-stable complex $RhCl[N(Ph)C(S)NMe_2](SCNMe_2)PPh_3$.

(Anal.: found: C, 54,8; H, 4.9; Cl, 5.1; N, 6.1; S, 9.1. $C_{30}H_{32}ClN_3PRhS_2$ calcd.: C, 53.9; H, 4.8; Cl, 5.3; N, 6.3; S, 9.6%, Mol. wt. osmometrically in $CHCl_3$, found: 664, calcd.: 668.)

Chloro(methyltrithiocarbonato)(N,N-dimethylthiocarboxamido)triphenylphosphinerhodium(III)

$RhCl(SMe)(SCNMe_2)(PPh_3)_2 \cdot C_6H_6$ is dissolved in CS_2. After 2 h the colour of the solution changes from dark red to orange and an orange precipitate is formed. Further precipitation results on addition of n-hexane. The product is washed with n-hexane and dried under vacuum. (Anal.: found: C, 45.6; H, 4.1; N, 2.2. $C_{23}H_{24}ClNPRhS_4$ calcd.: C, 45.1; H, 3.9, N, 2.3%.)

Results

All the complexes show the same characteristic infrared absorptions for the *N,N*-dimethylthiocarboxamido group (Table 1). They agree within a few cm^{-1} with the infrared absorptions for the thiocarboxamido group in $RhCl_2(SCNMe_2)(PPh_3)_2$ reported by Corain and Martelli [3]. They are listed, together with the infrared absorptions ascribed to the methylsulfido, the *N,N*-dimethyldithiocarbamato, and the *N,N*-dimethyl-*N'*-phenylthioureido group in Table 1.

Corain ascribes the vibration at 1653 cm^{-1} in IV to ν(C—N). This band is found between 1653 and 1675 cm^{-1} in the complexes I-III with a varying low intensity. Because of the constant high intensity (as expected for ν(C—N)) for the 1582-1608 cm^{-1} in I-IV we prefer to ascribe this band to a fundamental with a high degree of ν(C—N).

The IR absorptions of the methylsulfido group compare well with those reported for other methylsulfido complexes [8,9], e.g. $[Mn(CO)_4SMe]_2$: 2915w, 1428m, 1315w and 935w. The band expected in the region 1440-1415 [19] is probably obscured by a phosphine vibration.

The IR absorptions for the *N,N*-dimethyldithiocarbamato group are in agreement with those reported for other methyldithiocarbamato complexes [10-12]. The C—N stretching mode at 1524 cm^{-1} is comparable with that for $Rh^{III}(S_2CNMe_2)_3$ (1520 cm^{-1}) and $Rh^{I}(S_2CNMe_2)(PPh_3)_2$ (1520 cm^{-1} [13]. In the only other report of a *N,N*-dimethyl-*N'*-phenylthioureido complex [14] no IR absorptions have been given. We tentatively assign the 1565 cm^{-1} absorption to ν(C—N).

The bromine analogues of compounds I-III were prepared from $RhBr(PPh_3)_3$. The compounds were identified on the basis of their IR spectra, which were, except for the M—halogen vibrations, identical with the spectra of the chlorine compounds. The M—Cl absorptions, which could be assigned by comparison of the chlorine and bromine compounds, are listed in Table 2, together with the assigned M—S vibrations for the dithiocarbamato and the thioureido ligand.

The peak at 274 cm^{-1}, as found for II (Table 1) is ascribed to ω(CNC). It occurs in practically all *N,N*-dimethylthiocarbamates irrespective of the nature of the central metal [11]. The absorption at 292 cm^{-1} for the thioureido complex (III) could also be an almost pure ligand vibration. No M—N vibration could be assigned for III.

TABLE 1

CHARACTERISTIC IR FREQUENCIES (in cm^{-1})

CsI disks: br = broad, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

A. The N,N-dimethylthiocarboxamido group (SCNMe$_2$)									
RhCl(SMe)(SCNMe$_2$)(PPh$_3$)$_2$ (I)	1675vw	1582s	1408w	1400w	1225w	916w	838m	559w	330w
RhCl(S$_2$CNMe$_2$)(SCNMe$_2$)PPh$_3$ (II)	1666vw	1592s	[a]	[a]	1221w	919m	832m	560vw	330w
RhCl[N(Ph)C(S)NMe$_2$](SCNMe$_2$)PPh$_3$ (III)	1672vw	1608s	1410m		1222w	927m	837m	565vw	331w
RhCl$_2$(SCNMe$_2$)(PPh$_3$)$_2$[b] (IV)	1653m	1608s	1410(sh)	1400m	1220w	917m	826m	560vw	329w
B. The methylsulfido group (SMe)									
RhCl(SMe)(SCNMe$_2$)(PPh$_3$)$_2$ (I)	2900vw	1303w	943w						
C. The N,N-dimethyldithiocarbamato group (S$_2$CNMe$_2$)									
RhCl(S$_2$CNMe$_2$)(SCNMe$_2$)PPh$_3$ (II)	1524s(br)	1394s	1254w	1150 or 1155m(br)	1160m(br)	980w	581vw	274w	
D. The N,N-dimethyl-N′-phenylthioureido group (N(Ph)C(S)NMe$_2$)									
RhCl[N(Ph)C(S)NMe$_2$](SCNMe$_2$)PPh$_3$ (III)	1565s(br)	1361s	1203m	1110m	950w	788w	630w	292w	

[a] Obscured by dithiocarbamato vibration. [b] Reported by Corain and Martelli [3].

TABLE 2

METAL—CHLORINE AND METAL—SULFUR VIBRATIONS (cm^{-1})

CsI disks.

Complex	(M—Cl)	(M—S)
$RhCl(SMe)(SCNMe_2)(PPh_3)_2$ (I)	262, 223	[a]
$RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$ (II)	250	362
$RhCl[N(Ph)C(S)NMe_2](SCNMe_2)PPh_3$ (III)	252	356

[a] Not assigned.

TABLE 3

^1H NMR SPECTRA IN $CDCl_3$

τ in ppm, TMS internal standard, room temperature; c = centre of complex structure, s = singlet.

Complex	Phenyl protons	Thiocarboxamido protons[a]	Others[a]	
$RhCl(SMe)(SCNMe_2)(PPh_3)_2$ (I)	2.07 c	7.65(1) s	7.38(1) s	SMe
	2.70 c	7.92(1) s		
$RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$ (II)	2.36 c	6.98(1) s	6.89(2) s	S_2CNMe_2
	2.79 c	7.21(1) s		
$RhCl[N(Ph)C(S)NMe_2](SCNMe_2)PPh_3$ (III)	2.04 c	6.63(1) s		
	2.24-3.10[b]	7.10(3) s	7.10(3) s[c]	N(Ph)C(S)NMe2
$RhCl_2(SCNMe_2)(PPh_3)_2$ (IV)	2.07 c	7.67(1) s		
	2.65 c	7.91(1) s		

[a] Intensity ratios in parentheses. [b] Phenyl group of PPh_3 and Ph group of $N(Ph)C(NMe_2$. [c] N—CH_3 resonance of $SCNMe_2$ and $N(Ph)C(S)NMe_2$ coincide.

The ^1H NMR spectra of the complexes I-IV are summarized in Table 3. In all cases the *N,N*-dimethylthiocarboxamido group shows two methyl-proton resonances. As pointed out previously by Dean and Treichel (Mo and W; side-on coordination [5]) and Green and Angelici (Pt and Pd; coordination via C and C—S bridge [4]), this is caused by restricted rotation around the C—N bond. The N—CH_3 resonances of the dithiocarbamato group and those of the thioureido group coincide at room temperature.

Discussion

The two metal—chlorine vibrations for the methylsulfido complex suggest a dimeric structure via chloride bridges [20,21]. Because of the preference for 6-coordination of [Rh^{III}, *d*6] this implies that the thiocarboxamido group is coordinated via carbon only (Fig. 1, III). The precise configuration of the dimer is being further studied. In $CHCl_3$ solution complex I decomposes, resulting in the formation and precipitation of $RhCl_2(SCNMe_2)(PPh_3)_2 \cdot 2CHCl_3$, as shown by elemental analyses and the IR spectrum. This is confirmed by the NMR spectrum in $CDCl_3$ (Table 3). It shows the two signals of $RhCl_2(S_2CNMe_2)(SCNMe_2)PPh_3$ and a signal at $\tau = 7.38$ ppm of the reacted MeS group.

Chemical evidence for the presence of a methylsulfido group in I comes from the reaction of I with CS_2 (see Experimental). This leads to the formation of the methyltrithiocarbonato-thiocarboxamido complex $RhCl(S_2CSMe)(SCNMe_2)(PPh_3)$. The characteristic IR absorptions assigned to the methyltrithiocarbonato group (1510w, 1045vw, 1008m, 973s and 928m) agree well with those reported by Coucouvanis et al. [15] for (t-Bu—SCS_2) in $Fe(S_2CS(t\text{-}Bu))_3$; 1060, 1021 (C=S), 977 (SCS_2) and 921 (SCS_2).

CS_2 insertion into a M—SR bond has previously been reported for CuSR [18], $CpM(CO)_3SR$ and $[CpM(CO)_2SR]_2$ with M = Mo, W [16] and for $[CpNiSR]_2$ [17]. To our knowledge this is the first example of CS_2 insertion into a Rh—SR bond.

The one M—Cl vibration found for II as well as for III, together with the monomeric molecular weight in chloroform (see Experimental) suggests both complexes to be monomeric. In both cases the assigned M—S vibration implicates S-coordination for the $(XC(S)NMe_2)$-ligand. The shift of the methyl protons of the dithiocarbamato (= dtc) group in II (Table 3) is almost the same as the shift of the bidentate dtc-group in $Rh(S_2CNMe_2)_3PPh_3$ ($\tau = 6.72$) and $Rh(S_2CNMe_2)_3(CO)PPh_3$ ($\tau = 6.75$) and is clearly different from that of the unidentate dtc methylprotons ($\tau = 7.24$ and 7.22 ppm respectively) in the same complexes [13]. This suggests the dtc to be bidentate. Because of the preferred 6-coordination for Rh^{III}, the thiocarboxamido-group should be coordinated side-on via C and S, and the crystal structure determination confirms the suggested structure (Fig. 2).

Molecular structure of $RhCl(S_2SNMe_2)(SCNMe_2)PPh_3$

The geometry of the $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$ molecule in the monochloroform adduct is shown in Fig. 2. The most important bond distances and angles are shown in Table 4. Full details of structure determination will be published elsewhere [22].

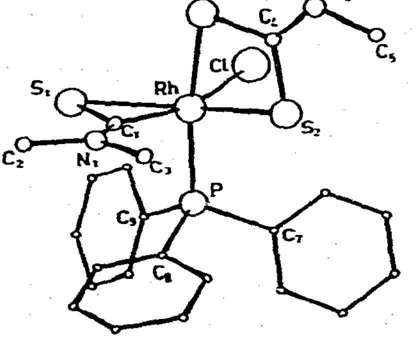


Fig. 2. Geometry of the $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$ molecule.

TABLE 4

RELEVANT BOND DISTANCES AND ANGLES

Bond distances (Å)		Bond angles (degrees)	
Rh—C(1)	1.895(16)	C(1)—Rh—Cl	154.7(5)
Rh—S(1)	2.432(5)	S(1)—Rh—S(2)	152.4(2)
Rh—S(2)	2.322(5)	Cl—Rh—S(2)	92.3(2)
Rh—S(3)	2.389(5)	S(1)—Rh—C(1)	42.2(5)
Rh—Cl	2.477(5)	Rh—C(1)—S(1)	86.7(7)
Rh—P	2.292(5)	Rh—S(1)—C(1)	51.1(6)
C(1)—N(1)	1.311(22)	S(3)—Rh—P	169.2(2)
C(1)—S(1)	1.638(16)		
C(4)—S(2)	1.704(17)		
C(4)—S(3)	1.678(16)		
C(4)—N(2)	1.337(21)		

The carbon atom of the thiocarboxamido group and S of the dithiocarbamato group are found in *cis* positions relative to each other. Because of the identical M—Cl vibrations of II and III (250 cm^{-1}, Cl *trans* relative to C) we suggest an analogous structure for the thioureido complex (Fig. 3) in which, because of the presence of only one PPh_3, the thioureido-ligand will be coordinated via N and S. This bonding situation has been proposed for $[Mn(CO)_3N(Ph)C(S)NMe_2]_2$ [14].

Compared with the side-on coordinated *N,N*-dipropylthiocarboxamido group in $[MoS(S_2CNPr_2)(SCNPr_2)]_2$ [7] the C—N and C—S distances and the angles N—C—S and C—M—S in our thiocarboxamido group are not significantly different. The nitrogen atom is essentially trigonal. The C—N distance (1.311 Å) is similar to the C—N distances in tertiary and secondary amino-carbene complexes (1.29-1.38 Å) [23] and typical organic amides [24]. This is in accordance with the hindered rotation around the C—N bond and shows the presence of substantial $p\pi$—$p\pi$ overlap.

The coordination geometry found is comparable with that for side-on coordinated allene complexes (cf. $RhI(H_2C{=}C{=}CH_2)(PPh_3)_2$ [25] and $Rh(acac)(Me_2C{=}C{=}CH_2)_2$ [26]) and for CS_2 complexes (cf. $Pt(CS_2)(PPh_3)_2$ [27] and $Pd(CS_2)(PPh_3)_2$ [28]). The C—S distance (1.638 (16) Å) is not significantly different from the C—S distance in the CS_2 complexes of Pt (1.72 (5) Å) and Pd (1.65 (3) Å). In all cases there is substantial distortion from trigonality for the metal-coordinated carbon. The Rh—C distance we found (1.895 Å) is shorter than those reported for Rh^I and Rh^{III} amino-carbene complexes (1.96-2.01 Å) [23, 29, 30] and for other Rh—C sp^2 bonds (1.96-2.00 Å) [31-33]. It is also shorter than the Rh—C distance in Rh—allene (2.04-2.07 Å) [25,26], Rh—alkene (2.13-2.19 Å) and perfluoralkene (2.00-2.03 Å) complexes [34,35]. It is about the same as the Rh—C distance in a Rh^{III} carbonyl compound (1.892 Å) [29]. The Rh—S(1) bond is significantly longer than the Rh—S(2) bond *trans* to it, which suggests substantially weaker bonding. The C(1)—S(1) distance reflects considerable multiple bonding, comparable to that in the S_2CNMe_2 fragment (Table 4). We have made an attempt to summarize the above facts in the resonance structures shown in Fig. 4.

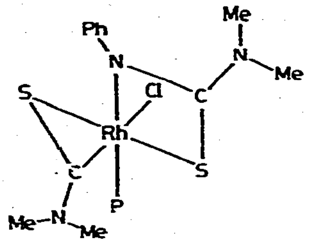


Fig. 3. Suggested structure for $RhCl(N(Ph)C(S)NMe_2)(SCNMe_2)PPh_3$.

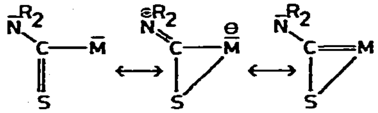


Fig. 4. Resonance structures for the side-on coordinated thiocarboxamido group.

The Rh—Cl distance in $RhCl(S_2CNMe_2)(SCNMe_2)PPh_3$ (2.477 (5) Å), showing the *trans*-influence of C(1), is intermediate to the Rh—Cl distance in the case of Cl *trans* to C(alkyl) in $RhCl(Py)_2[P(o\text{-tolyl})_2(o\text{-benzyl})]$ (2.531 (4) Å) [36] and Cl *trans* to C(carbene) in $RhCl_3(PEt_3)_2CHNMe_2$, (2.445 (3) Å) [23].

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